Metal impurities in LiF: opportunity for X-ray imaging detectors development

F. Somma[1*], P. Aloe[1], F. Bonfigli[2], R. M. Montereali[2], M. A.Vincenti[2], F. d'Acapito[3], S. Polosan[4]

1 Physics Dep., University of Roma Tre, V. della Vasca Navale 84, 00146 Roma, ITALY

2 ENEA C.R. Frascati, Photonic Micro and Nanostructures Laboratory, UTAPRAD-MNF V. E. Fermi 45, 00044 Frascati (Roma), ITALY

3 CNR-IOM-OGG, c/o ESRF BP220, GILDA CRG,6, Rue Jules Horowitz, 38043 Grenoble, FRANCE

4 National Institute of Materials Physics, Bucharest-Magurele 077125, ROMANIA

*e-mail: somma@fis.uniroma3.it

International Workshop on Extreme Ultraviolet Sources
University College Dublin,13-15 November 2010

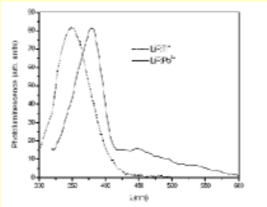
Introduction LiF crystals and films were proposed as novel extreme-ultraviolet (EUV) and X-ray imaging detectors based on the photoluminescence (PL) of colour centres. Several peculiar features of LiF-based detectors, like very high spatial resolution over a large field of view and wide dynamic range make them very promising as imaging plates for EUV and X-rays. An attractive opportunity in order to improve their performances is expected from metal-related defects embedded in a crystalline host matrix. Recently, it was shown that the presence of some impurities (Pb and Tl) into the raw LiF salts and crystals modifies the PL properties of stable F_2 and F_3^+ colour centres. The aim of this work is to study the influence of the metallic ion doping in the LiF matrix.

Samples Preparation

The starting LiF polycrystalline powder was prepared by using quasi-homogenous synthesis in aqueous solutions from high purity LiCl and ammonium fluorite (NH_4F). The powder was dried from 20 to 110 °C for 24 hours (in air). Un-doped, Pb^{2+} and Tl^+ doped LiF crystals were grown by using standard Kyropoulos growth technique in dry nitrogen atmosphere; PbF_2 and TlF salts were used for the doping. Several crystal slices, few mm thick, were successfully cleaved. Some slices were annealed at 300 °C for 64 hours (in dry nitrogen atmosphere) in order to eliminate the crystallization water. For the XAS studies, samples annealed at 450 ºC and 650 ºC were prepared in order to investigate the thermal stability of the Pb position in the crystals.

Optical Measurements

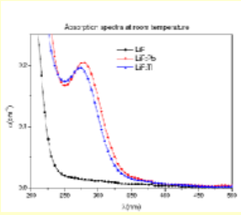
Optical Materials 32 (2010) 1309–1312, Physics procedia 2 (2209) 211-221



Optical absorption spectra at RT recorded on undoped, Pb^{2+}-doped (50 mg) and Tl-doped (500 mg) LiF crystals.

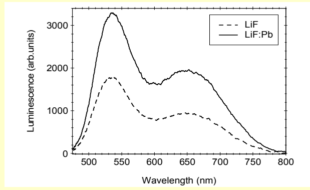
The optical absorption spectra shows a broad band located at 278 nm in a Pb-doped LiF crystals and at 273 nm for the Tl-doped crystals, obtained from the same LiF powder.

The absorption bands have been assigned to the A transition of the Pb^{2+} and Tl^+ ions.



RT normalized photoluminescence spectra of doped LiF crystals; the excitation wavelength is 273 nm for LiF:Tl and 278 nm for LiF:Pb crystals.

The PL spectrum of the Pb-doped LiF crystal, excited at 278 nm (4.47 eV) showed a broad and intense emission band peaking at about 375 nm (3.30 eV) accompanied by a much weaker and broader shoulder at about 465 nm (2.67 eV). The PL spectrum of the Tl-doped LiF crystal, excited at 273 nm (4.54 eV), has shown a broad and intense luminescence band peaking at about 350 nm (3.54 eV), with no other bands aside.



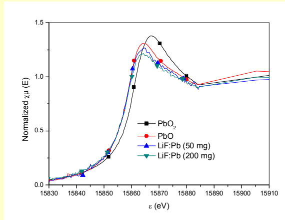
Photoluminescence spectra recorded at RT after X-ray irradiation of undoped crystal and Pb^{2+}-doped LiF crystal using excitation at 460 nm.The PL spectra show the typical broad emission bands of F_2 and F_3^+ peaked around 670 nm and 535 nm respectively.

X-ray irradiation of the samples was performed at RT under vacuum for about 20 min. by using a standard X-ray source equipped with an Al target (Al kα, E=1486.6eV).

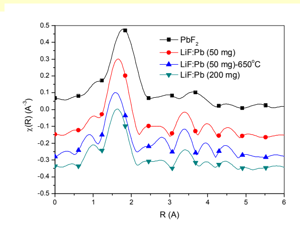
XANES and EXAFS Measurements

at GILDA CRG beamline , European Synchrotron Radiation Facility in Grenoble
Mat. Sci. And Eng, in press

The XANES spectra of LiF:Pb samples demonstrated that lead is in a 2+ valence state. The samples have the edge coincident with that of PbO and significantly shifted at lower energies respect to the PbO_2 compound. The EXAFS spectra are all markedly different from that of PbF_2, demonstrating that the precursor has undergone complete dissolution and that a new phase is really formed in the crystal. The first fluorine shell in the doped crystals has a shorter radius as derived from the shift of the first peak with respect to PbF_2. Then, the additional peak showed at about 3.5 Å means that there is a non-trivial atomic ordering also beyond the first shell, suggesting the incorporation of Pb in a crystalline environment. The increase of PbF_2 concentration in the melt or the thermal annealing processes do not lead to any visible rearrangement of the metal in the host matrix. *(Ravel B and Newville M 2005 J. Synchrotron Rad.* ***12*** *537)*



XANES spectra at the Pb-L_I edge of two samples (200 mg and 50 mg) compared with reference compounds PbO and PbO_2.

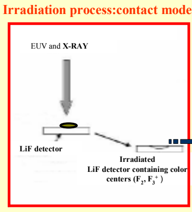


Fourier Transform (FT) of EXAFS spectra for the investigated samples compared with the model compound PbF_2. FT were carried out in the interval K = 2.2-9.0 $Å^{-1}$ with a k^2 weight.

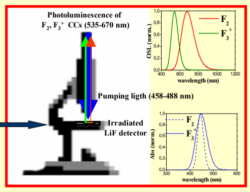
LiF-based X-ray imaging detectors

Novel lithium fluoride (LiF) imaging detectors for X-rays of energy from 20 eV to 10 keV have been recently proposed and successfully tested. Among the main peculiarities of the LiF-based detectors are intrinsic **high spatial resolution** on a **large field of view** and a **wide dynamic range**. Moreover they allow ease of use, as **insensitive to visible light**, and they need **no development process** after X-ray exposure, as the reading process is based on detection of the **visible photoluminescence of stable aggregate color centers** formed by the impinging radiation. They assure **great versatility**, as they can be grown in the form of thin films on different substrates by well assessed physical deposition techniques.

Irradiation process:contact mode



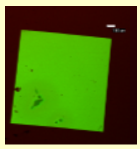
Readout process



Images stored in the irradiated LiF samples are observed by using optical microscopes in fluorescent mode. Irradiation with blue light excites the **visible photoluminescence of the F_2 and F_3^+ defects** locally created in the areas previously exposed to the X-ray beam. With appropriate laser excitation sources and time-resolved detection, the luminescence sensitivity maybe virtually unlimited: under suitable conditions even single luminescence center present in the sample can be detected.

Nuclear Instruments and Methods in Physics Research B 268 (2010) 3035–3039

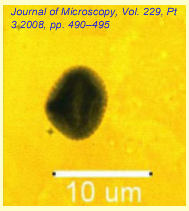
LiF crystal



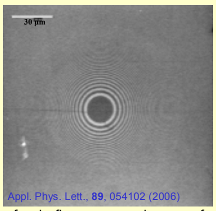
LiF film on Si (t=2.2micron)

The photo-induced signal coming from the LiF film on Si is significantly larger than the one coming from the LiF crystal. It is generally accepted that also the surface-to-volume ratios and the film compactness play a relevant role because they establish the density of the grain boundaries, which act as a source of vacancies during the color center formation and stabilization processes

Journal of Microscopy, Vol. 229, Pt 3,2008, pp. 490–495

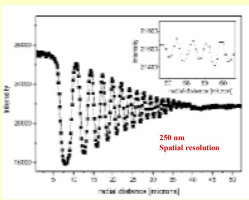


Confocal laser-scanning microscopy fluorescence image of a X-ray radiography of *Olea europaea* (*var. ascolana*) pollen grain stored on a LiF crystal with 20 shots of an Nd-YAG laser plasma source.



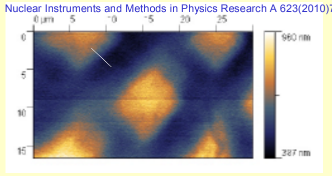
Appl. Phys. Lett., **89**, 054102 (2006)

Confocal fluorescence image of the phase Fresnel zone plate x-ray microradiograph stored on a 1.4micron thick LiF film grown on a glass substrate, under optical excitation at 458 nm. The brighter areas correspond to the x-ray most transparent zones.

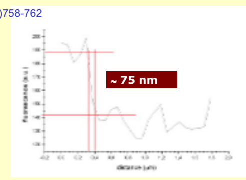


Data processing relative to the X-ray radiograph. The intensity is integrated in concentric circles and the result is plotted as a function of radius

Nuclear Instruments and Methods in Physics Research A 623(2010)758-762



SNOM optical image of a LiF film grown on a silicon substrate (thickness ~ 214 nm) irradiated by soft X-rays. The fluorescent pattern was obtained by masking LiF film with a copper mask.



Fluorescence intensity profile, traced along the white line.

Conclusions and perspectives

- ✓ The principal aim of our future work will be to improve the performances of an innovative bidimensional X- ray imaging detector based on doped LiF materials.
- ✓ Preliminary results confirm the possibility to increase PL signals of doped samples with respect to the undoped ones.
- ✓ Future developments are foreseen in the production of pure and doped LiF thin films as novel radiation detectors of increased sensitivity.
- ✓ Contact X-ray microscopy imaging results previously obtained by using LiF detectors encourage this investigation for X- ray single-shot *in vivo* experiments.